Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

CHARACTERIZATION OF PRODUCTS FROM THE UPGRADING OF SORBITOL USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND GAS CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED SPECTROMETRY

S. COULOMBE, G. JEAN, P. CHANTAL AND S. KALIAGUINE

OCTOBER 1985

This document is an unedited interim report prepared primarily for discussion and internal reporting purposes. It does not represent a final expression of the opinion of the Canada Centre for Mineral and Energy Technology (CANMET)

Ce document est un rapport provisoire non-révisé et rédigé principalement pour fin de discussion et de documentation interne. Il ne représente nullement l'expression définitive de l'opinion du Centre canadien de la technologie des minéraux et de l'énergie (CANMET)

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
DIVISION REPORT ERP/ERL 85-72 (IR)

MICROMEDIA

CHARACTERIZATION OF PRODUCTS FROM THE UPGRADING OF SORBITOL USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND GAS CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED SPECTROMETRY

S. COULOMBE*, G. JEAN*, P. CHANTAL** AND S. KALIAGUINE**

ABSTRACT

Products from the upgrading of sorbitol to hydrocarbons on zeolite ZSM-5 were analyzed using gas chromatography/mass spectrometry and gas chromatography/Fourier transform infrared spectrometry. Major individual compounds were identified and changes in the composition of products were assessed in view of the experimental conditions. Results showed that only low space velocity would favour the formation of aromatic hydrocarbons and that temperature had no significant effect from 350 to 450°C.

---

* Separation and Characterization Section, Hydrocarbon Processing Research Laboratories, Energy Research Laboratories, CANMET.

** Chemical Engineering Department, Laval University, Ste-Foy, Québec.

CARACTÉRISATION DES PRODUITS DE VALORISATION DU SORBITOL PAR CHROMATOGRAPHIE EN PHASE GAZEUSE/SPECTROMÉTRIE DE MASSE ET CHROMATOGRAPHIE EN PHASE GAZEUSE/INFRAROUGE À TRANSFORMÉE DE FOURIER

S. COULOMBE*, G. JEAN*, P. CHANTAL** ET S. KALIAGUINE**

RÉSUMÉ

Les produits de conversion du sorbitol sur zéolithe ZSM-5 ont été analysés par chromatographie en phase gazeuse/spectrométrie de masse (GC/MS) et par chromatographie en phase gazeuse/infrarouge à transformée de Fourier (GC/FTIR). Les composés majeurs ont été identifiés et les changements dans la composition des produits ont été examinés en fonction des conditions expérimentales. Les résultats montrent que seule une faible vélocité spatiale favorise la formation d'hydrocarbures aromatiques et que la température n'a pas d'influence significative entre 350 et 450°C.

---

* Section de séparation et de caractérisation, Laboratoire de recherche en valorisation des hydrocarbures, Laboratoires de recherche en énergie, CANMET.

** Département de génie chimique, Université Laval, Ste-Foy, Québec.

INTRODUCTION

Research on new sources for liquid fuels is necessary in view of the possible shortage of conventional sources in the future and the difficulties and high costs related to the production of liquid fuels from synthetic crude oils. Biomass is a possible source for the production of liquid fuels especially in the gasoline range as well as premium octane booster additives. Upgrading studies are performed at Laval University using biomass or biomass related model compounds for the production of new liquid fuels. This report summarizes the results of the characterization of products from the conversion of sorbitol under a variety of experimental conditions. This work will enable more information to be obtained on the reactions that are taking place on zeolite ZSM-5 and will also be relevant to the production of synthetic crudes from other feedstocks. It also allowed us to demonstrate the suitability of gas chromatography/mass spectrometry (GC/MS) and gas chromatography/Fourier transform infrared spectrometry (GC/FTIR) for the analysis of biomass synthetic fuels.

Samples were generated by Dr. S. Kaliaguine's research group at Laval University. After quantification of the products at Laval University, the samples were submitted to Energy Research Laboratories for characterization as part of a cooperative program initiated earlier (1). GC/MS and GC/FTIR were used to identify individual components and to assess the changes in the composition of the products in relation to the experimental conditions.

EXPERIMENTAL

The upgrading experiments were performed at Laval University using a zeolite ZSM-5 in the form of hydrogen which will be described in detail by reports from the Laval group. Briefly, the reactor was filled with 1 g of catalyst in a powder form which was not diluted. Sorbitol was mixed with water (2:1 w/w) and injected in the reactor at different space velocities. Figure 1 outlines the experimental conditions which cover temperatures from 350 to 450°C and space velocities from 0.5 to 2 LHSV. Helium was also fed to the reactor at approximately 6.5 to 7 mL/min. The reactor was operated at atmospheric pressure (P <2 psig). The products were collected as an aqueous solution which was extracted with chloroform prior to analysis.

The MS system consists of a Balzers QMG 511 quadrupole analyzer (electron impact mode) combined with an Incos data system. This system is attached to a Varian Vista 6500 gas chromatograph. The outlet of the GC column is positioned directly into the source for maximum transfer of sample to the MS source. The FTIR spectrometer is a Nicolet 60SX equipped with a Varian Vista 6000 gas chromatograph. Both chromatographs are equipped with a 60-m DB-5 capillary column for direct comparison of samples. The same temperature gradient was used in both cases, i.e., initial temperature of 60°C, increasing at 2°C/min. up to 220°C where it was held for 20 min. Most of the identification was done using the GC/MS system while GC/FTIR was used on some samples for confirmation.

RESULTS AND DISCUSSION

The identity of the products was confirmed with standard compounds when they were available. This was the case for cyclic molecules with low level of substitution. When standards were not available for the more substituted compounds, both GC/MS and GC/FTIR were used to confirm the identity of a number of molecules. However, the MS library contains over 30,000 compounds while the FTIR library only contains about 3,000 entries. Therefore, the small size of the FTIR library restricts the number of components that can be confirmed by both techniques. When confirmation was not possible, the GC/MS results generally gave enough information for a positive identification. For example, the molecular ion indicating the molecular weight and the retention time compared to a possible parent compound complement the spectrum itself in order to identify a peak. One drawback is that MS spectra could not always identify isomers which can be done more easily with FTIR. Table 1 lists the major components that have been identified and their occurrence in the six samples analyzed plus a blank run performed on glass beads. Question marks indicate where identification could not be achieved with the spectra alone because of the small concentration. In this case, some similarity with the spectrum of a peak occurring at the same relative retention time in other samples gave an indication of its identity. One can also notice the presence of two unknowns of relatively high concentration (peaks 35 and 37) that could not be identified.

Figures 2, 3 and 4 show the ion chromatograms (from the mass spectrometer computer) corresponding to the various samples. Samples 1, 3, 4 and 6 in Table 1 and Figure 2 show the influence of the temperature on the products (3 and 4 are replicates of the same conditions). It can be seen that the nature of the components is very similar regardless of the temperature. The major compounds are furan-type structures with some phenols and cyclic ketones. However, some hydrocarbons are produced, namely naphthalene and short-chain alkyl naphthalenes. It is interesting to note that the only noticeable hydrocarbons are two-ring structures like naphthalenes with some traces of indanes and indenes. Nevertheless, the overall effect of temperature on the nature and relative intensity of products is not very critical from 350 to 450°C at 1 LHSV. Figure 3 gives the products obtained with a blank run done at 400°C and a 1 LHSV on glass beads. These compounds are mainly furan-type molecules along with phenol. Thus the thermal decomposition of sorbitol gives some of the major products noted in the runs with catalyst, except for methyl furan (peak 6). Also in the blank run no compounds of molecular weight higher than 160 g/mol were detected.

Figure 4 shows the influence of space velocity on the nature of the products. There is not much difference between 1 and 2 LHSV. The same decomposition products already identified above are present. There seem to be more small peaks in the case of 1 LHSV. For example, indanes and indenes are absent at 2 LHSV. In this regard, the run performed at 2 LHSV is closer to the blank run as could be expected. However, as shown in Table 1, there is a definite difference for the products obtained at 0.5 LHSV. The nature of the components is radically different. Except for small amounts of phenols, there are virtually no oxygen compounds and the major products are mainly alkyl benzenes along with small quantities of naphthalenes and indanes. Thus it appears that the conversion of sorbitol to hydrocarbons is best performed at a longer reaction time.

CONCLUSIONS

From our results it appears that space velocity is a very critical parameter for the conversion of sorbitol to hydrocarbons. Only a longer contact time seems to promote the formation of alkyl benzenes. At higher space velocities only oxygen compounds, mainly furan-type molecules, cyclic ketones and phenols, are produced. Temperature does not seem to be a very critical parameter between 350 and 450°C.

This work allowed us to assess the suitability of GC/MS and GC/FTIR for the analysis of biomass synthetic fuels. Both techniques gave equivalent results with the FTIR being especially useful to confirm the functionality of the compounds. The small size of the FTIR library was however identified as a serious limitation of GC/FTIR. This library contains only 3,000 compounds compared with 31,000 for the MS library. Work will be undertaken to build a library in house which will be appropriate for the oil industry.

REFERENCES

1. Jean G., Coulombe S. and Sawatzky H., "Système de coopération", Division report ERP/ERL 84-12(OP), CANMET, Energy, Mines and Resources Canada, April 1984.

Table 1 - Identification of major compounds in products of conversion of sorbitol

Peak #	Compounds	1 Temperature: 350°C Space Velocity: 1LHSV	2 400°C 2LHSV	3 400°C 1LHSV	4 400°C 1LHSV	5 400°C 0.5LHSV	6 450°C 1LHSV	BLANK 400°C 1LHSV	*
1	Toluene				?	+			a
2	Cyclopentanone	+		+	+				b
3	1,1-diethoxyethane		+	+			+		c
4	3-pentanone		+				+	+	b
5	Furfural	+	+	+	+		+	+	b
6	2-methyl furan	+	+	+	+		+		b
7	4-penten-2-one						+		c
8	Ethyl benzene					+			c
9	Xylene	+		+	+	+			a
10	Xylene	+		+		+			a
11	1-(1-methylethoxy) propane			+					c
12	2-methyl 2-cyclopenten-1-one			+					c
13	1-(2-furanyl) ethanone	+	+	+	+		+	+	b
14	2-cyclohexen-1-one			+					c
15	5-methyl 2(5H) -furanone	?	+	+	+				b
16	2,3-pentanedione							+	b
17	Ethyl methyl benzene					+			c
18	5-methyl furfural	+	+	+	+		+	+	b
19	Trimethyl benzene					+			c
20	Phenol	+	+	+	+	+	+	+	a
21	C3-benzene	+		+		+	+		c
22	Benzofuran			+					a

Table 1 - Identification of major compounds in products of conversion of sorbitol (Cont'd)

Peak #	Compounds	1 Temperature: 350°C Space Velocity: 1LHSV	2 400°C 2LHSV	3 400°C 1LHSV	4 400°C 1LHSV	5 400°C 0.5LHSV	6 450°C 1LHSV	BLANK 400°C 1LHSV	*
23	5-methyl 3-hexen-2-one or 3,4-dimethyl 3-penten-2-one	+	+	+	+		+		c
24	2,5-diethoxy tetrahydrofuran							+	b
25	Trimethyl benzene					+			c
26	3-methyl 2-cyclohexen-1-one	?	?	+	?		+		c
27	Indane	?		+		+	+		a
28	2-hydroxy 2-cyclopenten-1-one	+	+	+	+				c
29	Tetrahydro pyran-2-methanol	+	+	+	+				c
30	Indene						+		c
31	2-methyl phenol	+		+	+		+		c
32	Ethyl dimethyl benzene					+			c
33	Unknown	+	+	+	+				
34	3-methyl phenol	+	+	+	+	+	+		c
35	Unknown	+		+			+		
36	Ethyl dimethyl benzene					+			c
37	Methyl benzofuran or 3-phenyl 2-propenal	+		+	+		+		c
38	C4-benzene					+			c
39	C4-benzene					+			c
40	Methyl indane	+		+	+	+	+		c
41	C4-benzene					+			c

Table 1 - Identification of major compounds in products of conversion of sorbitol (Cont'd)

	1	2	3	4	5	6	BLANK	
Temperature:	350°C	400°C	400°C	400°C	400°C	450°C	400°C	
Space Velocity:	1LHSV	2LHSV	1LHSV	1LHSV	0.5LHSV	1LHSV	1LHSV	*
Peak # Compounds								
42 Methyl indane	+		+	+		+		c
43 Methyl indene	+		+	+		+		c
44 Naphthalene	+	+	+	+	+	+		a
45 C5-benzene					+			c
46 Quinoline ?		+	+					
47 Dimethyl indane					+			c
48 Dimethyl indene	+		+			+		c
49 Methyl tetralin					+			c
50 Substituted benzene					+			c
51 Methyl naphthalene	+	+	+	+	+	+		c
52 Methyl naphthalene	+		+	+	+	+		c
53 Ethyl naphthalene	+		+	+		+		c
54 Dimethyl naphthalene	+	+	+	+	+	+		c
55 Dimethyl naphthalene				+	+			c
56 Dimethyl naphthalene				+	+	+		c
57 Dimethyl naphthalene				+				c
58 C3-naphthalene				+	+			c

---

* indicates the mode of identification: a-pure compounds, b-MS and FTIR libraries, c-MS library only.

+ indicates presence of compound.

? indicates possible identification. Peaks 53 to 58 are minor components of higher retention time than shown in Figures 2, 3 and 4.

FIGURE CAPTIONS

Fig. 1- Outline of experimental conditions for the upgrading of sorbitol. Experiments are identified by the numbers. B = blank run performed on glass beads.

Fig. 2- Reconstituted ion chromatograms from GC/MS showing the influence of temperature on the composition of products. Space velocity = 1 LHSV. Samples 3 and 4 are replicates of the same conditions. Refer to Table 1 for peak identification.

Fig. 3- Reconstituted ion chromatogram from GC/MS of the products obtained from a blank run performed on glass beads. Refer to Table 1 for peak identification.

Fig. 4- Reconstituted ion chromatograms from GC/MS showing the influence of space velocity on the composition of the products. Temperature = 400°C. Samples 3 and 4 are replicates of the same conditions. Refer to Table 1 for peak identification.

Fig 1

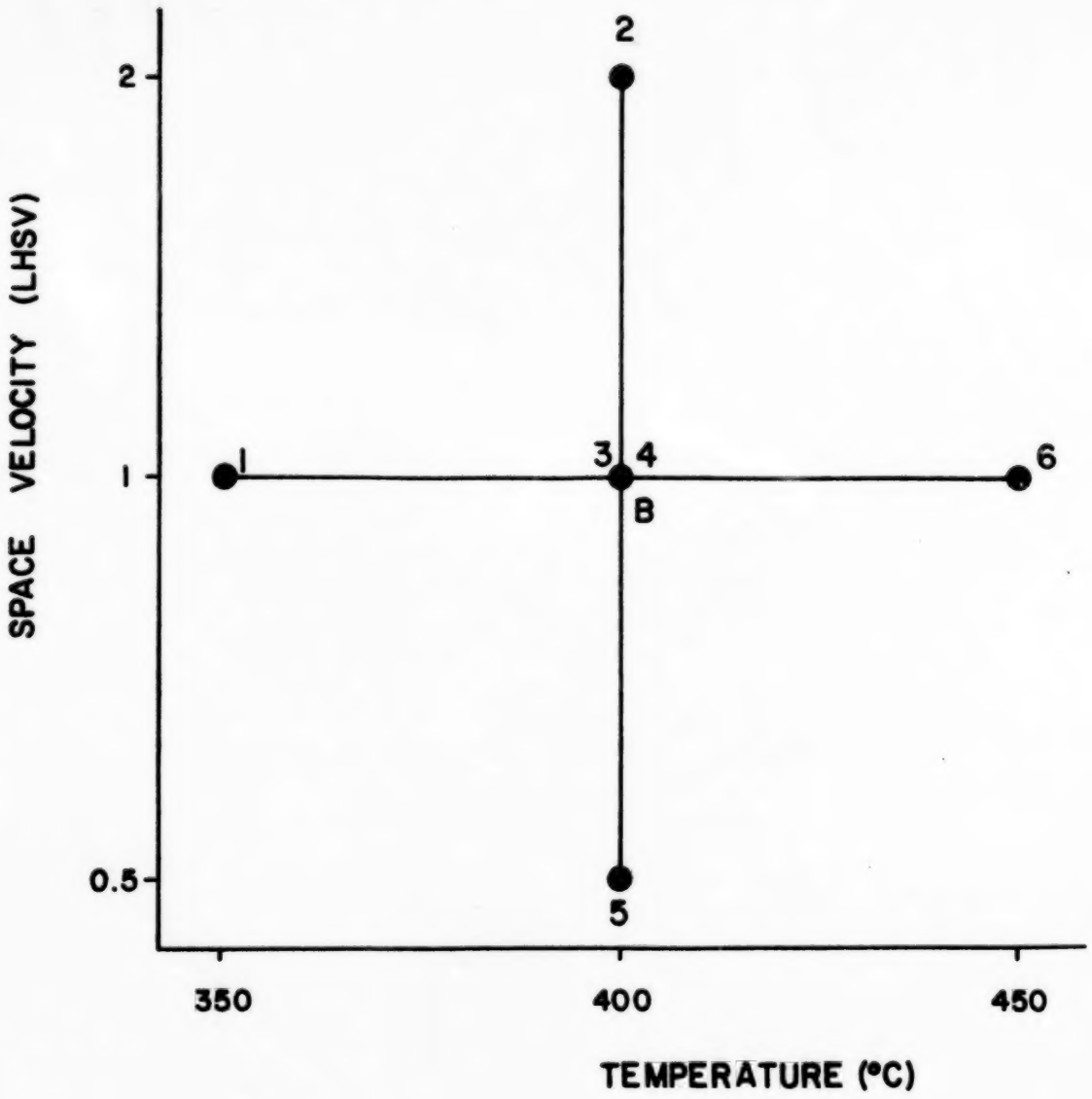
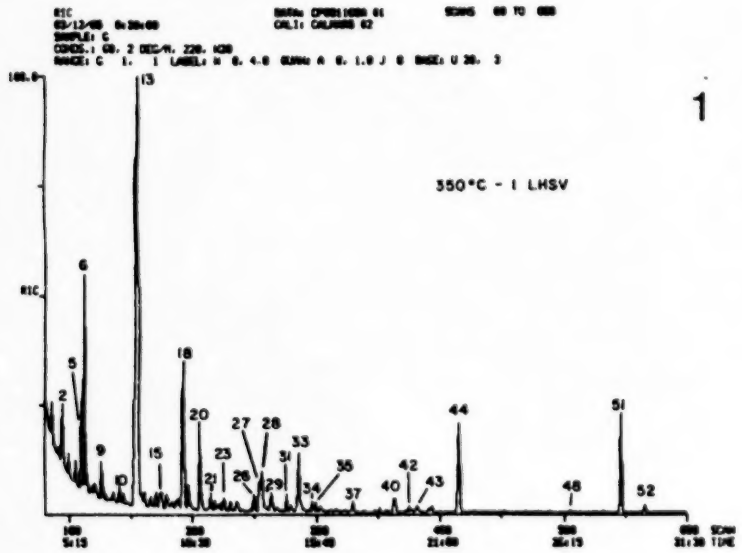
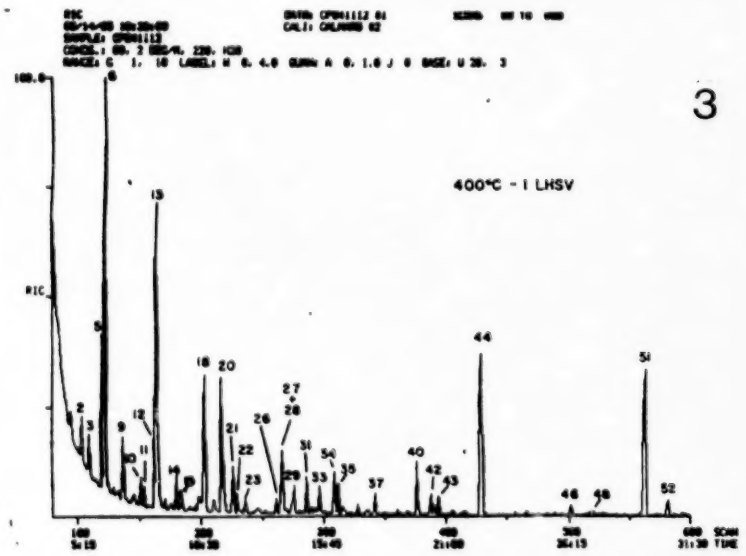
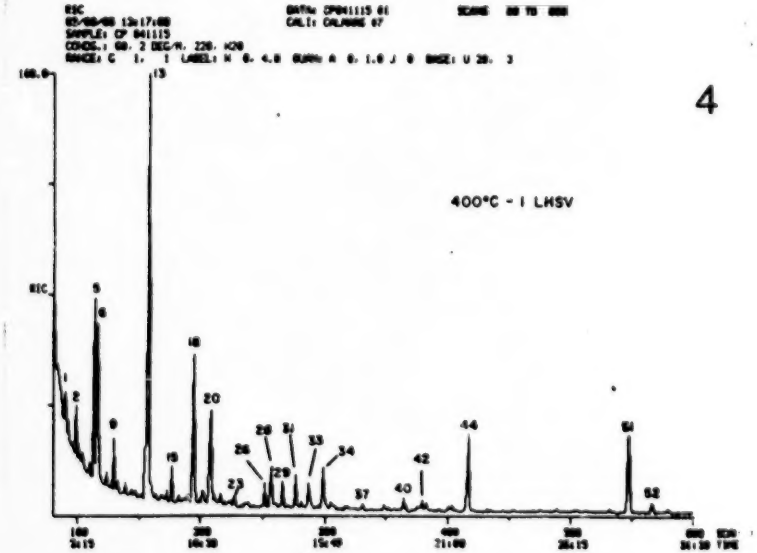

2
2
1
0.5
SPACE VELOCITY (LHSV)
1
2
3
4
5
6
B
350
400
450
TEMPERATURE (°C)

Fig 2


1
350°C - 1 LHSV
RIC


3
400°C - 1 LHSV
RIC


4
400°C - 1 LHSV
RIC

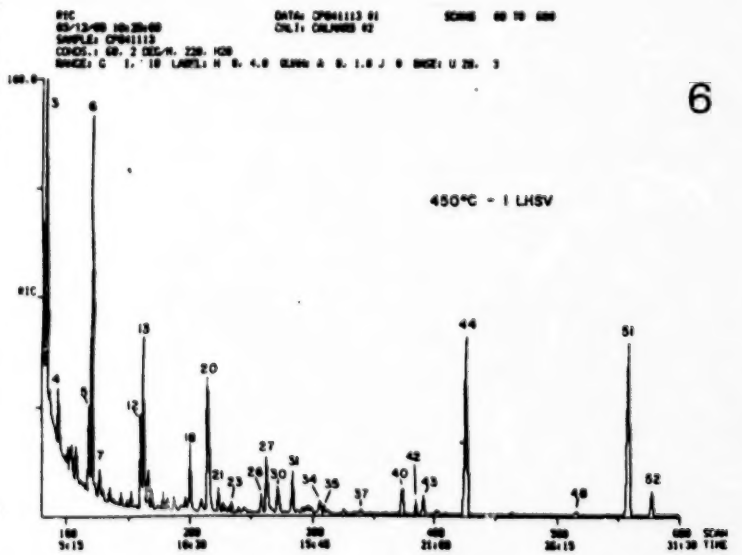
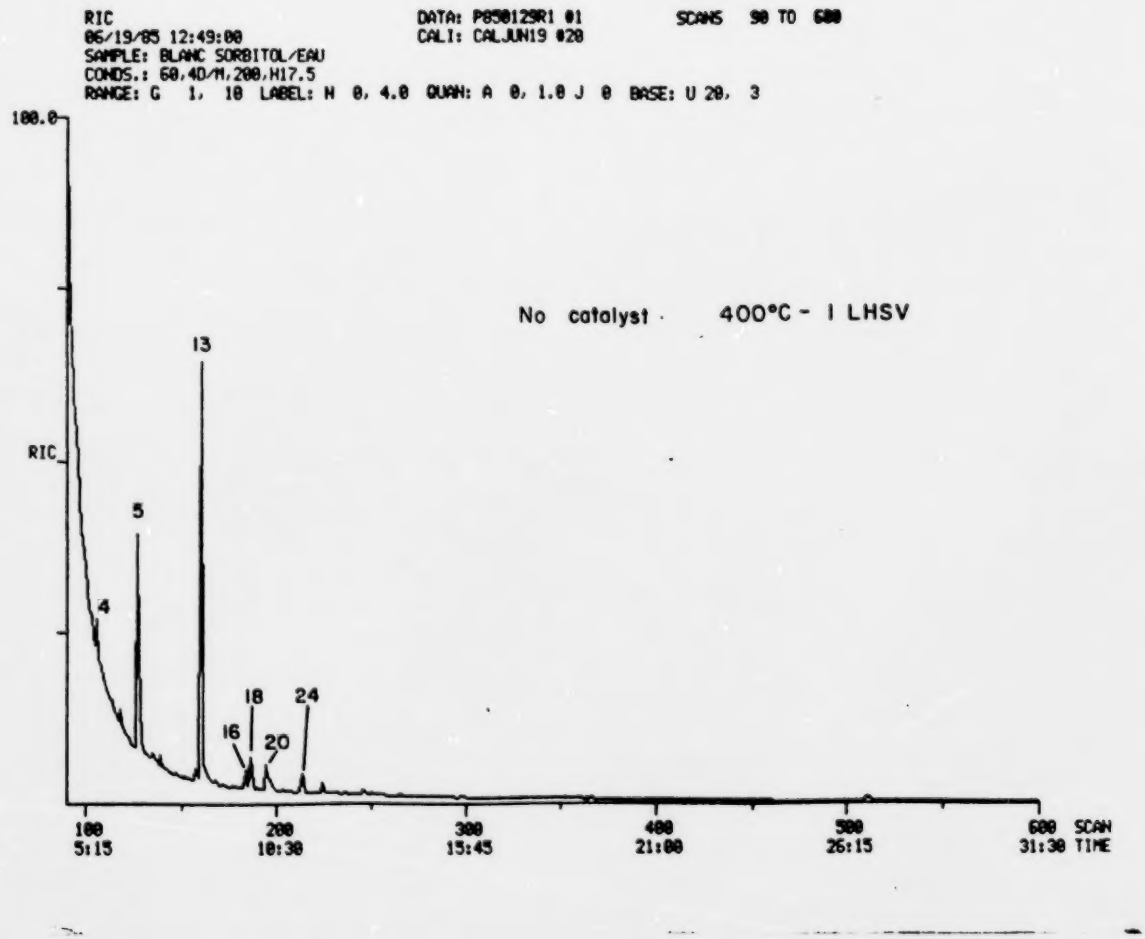

6
450°C - 1 LHSV
RIC

Fig 3


RIC
06/19/85 12:49:00
SAMPLE: BLANC SORBITOL/EAU
CONDS.: 60,40/M,200,H17.5
RANGE: G 1, 10 LABEL: N 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3
DATA: P850129R1 01
CALI: CALJUN19 020
SCANS 90 TO 600
No catalyst · 400°C - 1 LHSV
100.0
RIC
13
5
4
18
24
16
20
100
5:15
200
10:30
300
15:45
400
21:00
500
26:15
600 SCAN
31:30 TIME

F. 4